SYNTHESIS OF FEW-LAYER, LARGE AREA HEXAGONAL-BORON NITRIDE BY PULSED LASER DEPOSITION (POSTPRINT)

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14. ABSTRACT
Pulsed laser deposition (PLD) has been investigated as a technique for synthesis of ultra-thin, few-layer hexagonal boron nitride (fi-BN) thin films on crystalline highly ordered pyrolytic graphite (HOPG) and sapphire (0001) substrates. The plasma-based processing technique allows for increased excitations of deposited atoms due to background nitrogen gas collisional ionizations and extended resonance time of the energetic species presence at the condensation surface. These processes permit growth of thin, polycrystalline h-BN at 700 °C, a much lower temperature than that required by traditional growth methods. Analysis of the as-deposited films reveals epitaxial-like growth on the nearly lattice matched HOPG substrate, resulting in a polycrystalline fi-BN film, and amorphous BN (α-BN) on the sapphire substrates, both with thicknesses of 1.5–2 nm. Stoichiometric films with boron-to-nitrogen ratios of unity were achieved by adjusting the background pressure within the deposition chamber and distance between the target and substrate. The reduction in deposition temperature and formation of stoichiometric, large-area fi-BN films by PLD provide a process that is easily scaled-up for twodimensional dielectric material synthesis and also present a possibility to produce very thin and uniform α-BN.

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Synthesis of few-layer, large area hexagonal-boron nitride by pulsed laser deposition

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ABSTRACT

Pulsed laser deposition (PLD) has been investigated as a technique for synthesis of ultra thin, few layer hexagonal boron nitride (h BN) thin films on crystalline highly ordered pyrolytic graphite (HOPG) and sapphire (0001) substrates. The plasma based processing technique allows for increased excitations of deposited atoms due to background nitrogen gas collisional ionizations and extended resonance time of the energetic species presence at the condensation surface. These processes permit growth of thin, polycrystalline h BN at 700 °C, a much lower temperature than that required by traditional growth methods. Analysis of the as deposited films reveals epitaxial like growth on the nearly lattice matched HOPG substrate, resulting in a polycrystalline h BN film, and amorphous BN (a BN) on the sapphire substrates, both with thicknesses of 1.5 2 nm. Stoichiometric films with boron to nitrogen ratios of unity were achieved by adjusting the background pressure within the deposition chamber and distance between the target and substrate. The reduction in deposition temperature and formation of stoichiometric, large area h BN films by PLD provide a process that is easily scaled up for two dimensional dielectric material synthesis and also present a possibility to produce very thin and uniform a BN.

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1. Introduction

Two dimensional (2D) hexagonal boron nitride (h BN) has been investigated for use in nanotechnology applications including high speed transistor devices [1,2], flexible electronics [3,4], and high temperature coatings [5,6]. Structurally similar to graphene, h BN nanosheets consist of alternating B and N atoms arranged in a sp^2 bonded hexagonal lattice structure in plane, with van der Waals interactions between the layered sheets. The h BN sheets exhibit desirable properties including a wide band gap, high temperature stability, and inertness to many chemical environments. Boron nitride is a complementary dielectric material to graphene in 2D nanoelectronic devices as it provides an atomically smooth surface free of dangling bonds, high surface optical phonon modes, a good tunneling barrier for electrons, and minimal sites for adsorbed surface impurities [7]. The use of exfoliated h BN as a substrate dielectric material in graphene devices has been shown to markedly increase electron mobility in graphene by several times when compared to traditional dielectric materials such as thermally grown silicon dioxide [8].

Current methods for preparation of h BN nanosheets include mechanical and chemical exfoliation [9 12], high temperature chemical vapor deposition (CVD) [13 16], and PVD techniques including reactive sputtering followed by high temperature annealing [17] and pulsed laser deposition (PLD) of boron nitride nanosheets [18]. Mechanically exfoliated h BN flakes have been used for device level testing of numerous configurations incorporating graphene and other two dimensional materials, but the device size is limited to the size of the flake and the exfoliation thickness is not well predictable, which hinders scale up for device fabrication. Most of the CVD routes for h BN growth include the use of metal substrates or catalysts. Only recently, a direct growth of polycrystalline few layer h BN on sapphire and silicon substrates using CVD techniques was successfully demonstrated with a deposition of polyborazylene film at moderate temperatures and subsequent conversion to h BN by annealing at 1000 °C [16]. This also includes recent reports on the direct CVD growth of h BN on the surface of epitaxial graphene with an ammonia borane precursor in a vertical tube furnace at 1075 °C [19].

Clearly, one major challenge for large area, 2D h BN material synthesis is the reduction of the growth or annealing temperatures. Alternatively, growth of 2D materials by means of physical vapor deposition (PVD) may offer such a possibility, as these processes involve energetic plasmas which can add to the surface adatom mobilities and create

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conditions for h BN growth at lower synthesis temperatures. The at tempts with reactive sputtering [17] are promising but yielded amor phous materials which were converted to crystalline BN with the 850 °C anneal, similar to the CVD routes described above.

Pulsed laser deposition (PLD) is an alternative PVD technique to re active sputtering, where a high energy, focused laser beam pulse causes rapid heating on the face of the target, causing both ionized and neutral components to accelerate from the target in the form of a plasma plume normal to the target surface. The plasma plume propagates in the direc tion of the substrate and can be thermalized by collisions with the back ground gas, depending on the pressure and target to surface distance. The resulting film quality and composition on the substrate can be af fected by parameters including laser wavelength, power, pulse rate, pulse duration, target to substrate working distance and relative orien tation, background gas type and pressure, and substrate temperature. Whereas alternative PVD techniques present difficulties in preparing complex stoichiometric films due to differing partial pressures of the in dividual species in the vapor phase, PLD has proven useful in preparing complex thin films due to the rapid, localized heating, and relatively stoichiometric plasmas expelled from the target. This technique has also proven viable for growth of thicker boron nitride films of different crystalline orientations including hexagonal and cubic phases [20], at relatively low temperatures of 650 °C with B:N ratios of approximately one. Nanoscale thicknesses of h BN were synthesized using a high powered CO_2 pulsed laser and showed a possibility of a reduction of substrate temperature for deposition to around 400 °C, and formation of overlapping boron nitride nanosheets [18,21]. The nanosheets, how ever, were non uniform in thickness and morphology over large areas, limiting their ability to be used for electronic applications. Here, growth of ultra thin (less than 2 nm) stoichiometric, crystalline hexagonal phase boron nitride by means of pulsed laser deposition is discussed.

2. Experimental

Few layer boron nitride films were deposited in an ultra high vacu um chamber with residual base pressures of 2×10^{-9} Torr. Ablation from an amorphous boron nitride target (99.99% pure) was carried out using a Lambda Physik LPX300 248 nm KrF excimer laser at pulse energies of 900 mJ/pulse, 30 ns duration, and 1 Hz repetition rate. A fo cusing lens reduced the laser spot size to an area of 2.66 mm × 1.50 mm with a flux of 22.5 J/cm^2 upon impact with the target. A 1000 W Astex ECR power supply supplied heat to the substrate by means of joule heating a tungsten filament to a sample temperature of 700 °C, calibrat ed using a thermocouple spot welded on the block just beneath the substrate. After heating each sample to the appropriate temperature, the target was cleaned by laser ablation to remove any adsorbed impu rities on the target surface, while the deposition sample stage was cov ered with a shutter. Depositions were performed in nitrogen background gas, where pressure was controlled by a butterfly valve to preset values within 10^{-4} to 50 mTorr range and keeping the flow of ultra high purity nitrogen gas (99.9999%) at 30 sccm. After deposition, the substrate was allowed to cool to room temperature before removal from the vacuum chamber. A schematic of the deposition chamber and process is shown in Fig. 1. Two different target to substrate working distances of 1 cm and 3 cm were used in the study, with the plume at 45° to the substrate surface. Films were grown for 1 s at the 1 cm work ing distance, and 5 s at 3 cm working distance, in order to achieve the same thickness of BN films.

To guide the PLD process toward the formation of h BN films at re duced substrate temperatures, the ablated plasma dynamic was cap tured by collecting images of spatial, broadband plasma emission intensities timed from the laser impact on the target. A high speed Princeton Instruments 576 S/RBE ICCD camera with a 2 ns resolution in gate control was used to collect distributions of emitting species timed to the laser pulse with 100 ns steps and 100 ns gate widths. Plas ma images were recorded for all visible emission within 300 900 nm

(limited by window and camera bandwidths) with no image averaging, and each image corresponding to a single laser shot.

Highly ordered pyrolytic graphite (HOPG) and sapphire samples with (0001) surface termination and dimensions 5 mm × 5 mm provid ed atomically smooth surfaces with different lattice constants and elec trical properties for deposition substrates. Structurally, HOPG (a axis lattice constant of 0.246 nm) is very similar to h BN, with a lattice mis match of less than 2% and similar interlayer spacing. In order to create a clean sp^2 bonded carbon face on the substrate, exfoliation of several layers of material occurred immediately prior to placing in the deposi tion chamber. Polished sapphire (0001) substrates provide an ultra smooth, highly crystalline, insulating interface and are used as a sub strate material in many transistor fabrications. While c axis oriented sapphire also provides a hexagonal planar template, the sapphire in plane a axis lattice constant is 0.476 nm, which is almost twice that of h BN (0.250 nm). Heating the substrate to 700 °C during deposition eliminated all but a minimal amount of adsorbed oxygen contamination on both substrates.

In order to assess film composition, X ray photoelectron spectroscopic (XPS) analysis was carried out using a Kratos AXIS Ultra spectrometer with a monochromatic Al Kα x ray source (1486.7 eV) operated at 120 W (12 kV, 10 mA) and at approximately 4×10^{-9} Torr. In this system, the analyzer is oriented at 90° relative to the sample surface. Survey scans were collected over the binding en ergy range of −5 to 1200 eV, in 1 eV steps, using a dwell time of 300 ms and an analyzer pass energy of 160 eV. High resolution spectra of the B 1s, N 1s, O 1s, and C 1s regions were acquired using an energy step size of 0.1 eV, a dwell time of 500 ms, and an analyzer pass energy of 20 eV. Since BN is an insulator, a low energy electron flood source was utilized for charge compensation in cases where differential surface charging was observed. XPS spectra were analyzed using the CasaXPS software. The binding energy scale was calibrated to the C 1s peak from adventitious carbon at 284.8 eV. The atomic concentration of oxygen atoms was corrected by subtracting the O 1s contributions from adventitious carbon contamination and from the underlying sapphire substrate (O:Al for clean sapphire measured on this spectrom eter was approximately 1.5) [22]. Peak areas were determined using a Shirley background subtraction, and atomic concentrations were calculated by applying relative sensitivity factors specific to the XPS in strument. Curve fits for the B 1s and N 1s peaks were obtained by fitting the peaks with a Gaussian Lorentzian function with a 30% Lorentz contribution.

To determine structural and electrical properties, the films were ex amined with Raman spectroscopy, AFM topography, TEM, and conduc tive atomic force microscopy (C AFM). Raman structural measurements
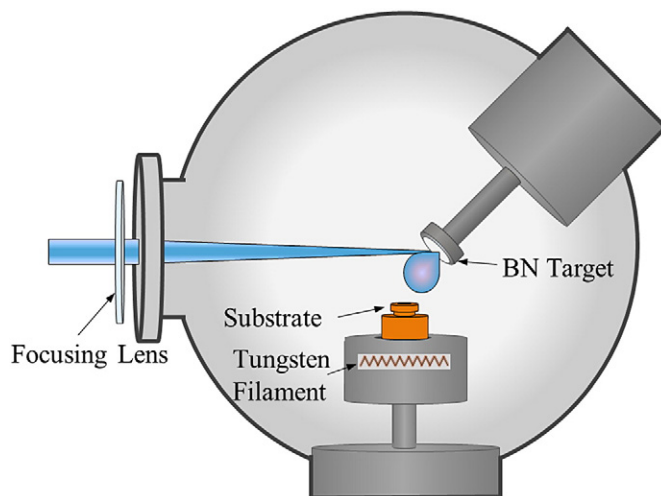

Fig. 1. Schematic of PLD setup.

were performed using a Renishaw Raman system with an Ar ion laser at 514 nm and 8 mW input power. AFM topographical images of *h* BN on HOPG and sapphire were acquired using a Bruker Dimension Icon AFM. For these measurements, the AFM was operated in tapping mode using an AFM tip with a nominal radius of curvature of ~2 nm (SNL 10, Bruker). Conductive atomic force microscope (CAFM) measurements were used to verify large area and pin hole free *h* BN films grown on the conductive HOPG substrate, and to determine tunneling performance at various locations on the film. Scans were taken using a doped diamond probe (DDESP 10, Bruker) to avoid tip wear, and electrical current between the biased tip and the grounded HOPG substrate was recorded using a current amplifier having a sensitivity of 1 nA/V.

3. Results and discussion

Altering the working distance as well as changing the background gas pressure within the chamber strongly impacts the incoming plasma energies and local composition in the PLD process. In particular, extending the working distance and increasing background pressure maximize the probability of collisions between ablated plasma species and background gas, reducing the incoming plasma energies by thermalization, and allowing for a longer reaction time of the energetic ablated species with the background gas species [23]. Depending on the laser energy and target material, there is an optimum pressure distance parameter space beyond which the plumes will be fully thermalized without reaching the substrate location, and the benefits of the energetic plasma growth as compared to a CVD will be lost.

Fig. 2 shows a series of images taken at 3 cm target to substrate working distance, depicting broadband plasma emission intensities as a function of time and background pressure of ultra high purity nitrogen gas. At 600 ns after the laser impacts the target, the plume dynamics appear to be fairly similar across the range of pressures examined in this study (10^{-4} mTorr, 5 mTorr, and 50 mTorr). Significant differences are evident at 1200 ns, when the plume is spatially confined due to collisions with o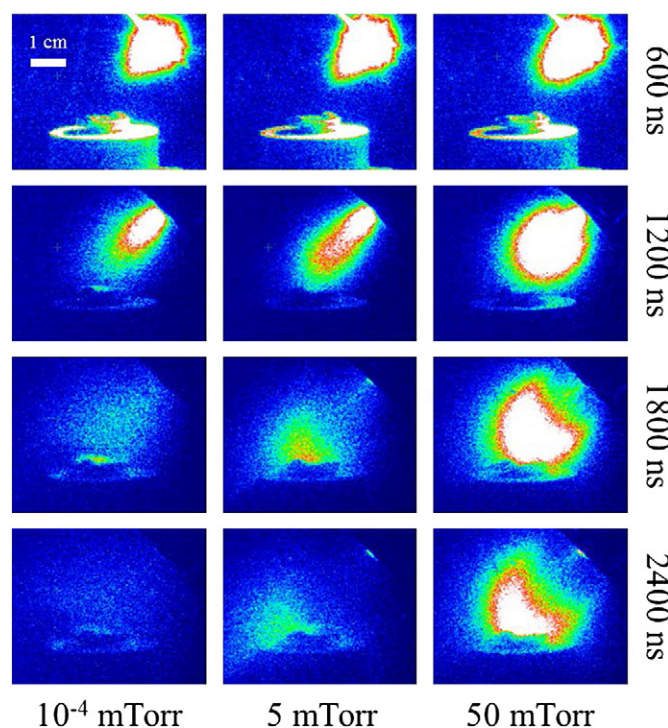ther gas molecules inside of the plume and at the plume boundary. At 1800 ns and 2400 ns, plasma confinement is observed at 50 mTorr, in contrast to the diffuse, unconfined plume that has nearly dissipated entirely at the same times at 10^{-4} mTorr. Such plasma confinement is well known for plasma conditions leading to the formation of clusters and radical species from both target atoms and reactive background gas [24].

Furthermore, Fig. 2 clearly shows the additional excitations of the energetic plasma plume with the substrate. This additional plasma excitation at the substrate surface lasts for relatively long times and with a much stronger intensity when the background pressure is increased. The energetic plume lasted as long as 4 μs after the laser pulse at a pressure of 50 mTorr. Such conditions create the extended presence of chemically reactive species (e.g. atomic boron and nitrogen), and possibly their radicals with increased vibrational temperatures at the film condensation surface. This is supported by earlier reports on PLD process optimization for a low temperature growth of ceramic and fullerene structures, where plume collisions with the substrates provided reactive species and high vibration energy radicals for increased adatom mobility, extended surface diffusion times, and reactivity needed for the formation of crystalline films at low substrate temperatures [25,26]. For the shorter working distances, similar plasma plume evolution processes were observed as in Fig. 2, but plumes had much less time for collisional reactions with the background gas before reaching the substrate surface.

Representative high resolution spectra of the B1s and N1s regions are shown in Fig. 3a and b. The B 1s peak is fit with two components at 190.6 eV and 192.1 eV, corresponding to BN and BN_xO_y, respectively. The small amount of BN_xO_y observed as a shoulder on the B 1s spectra is seen in other polycrystalline *h* BN films [16], and is most likely due to exposure to ambient conditions and oxidation at the polycrystalline
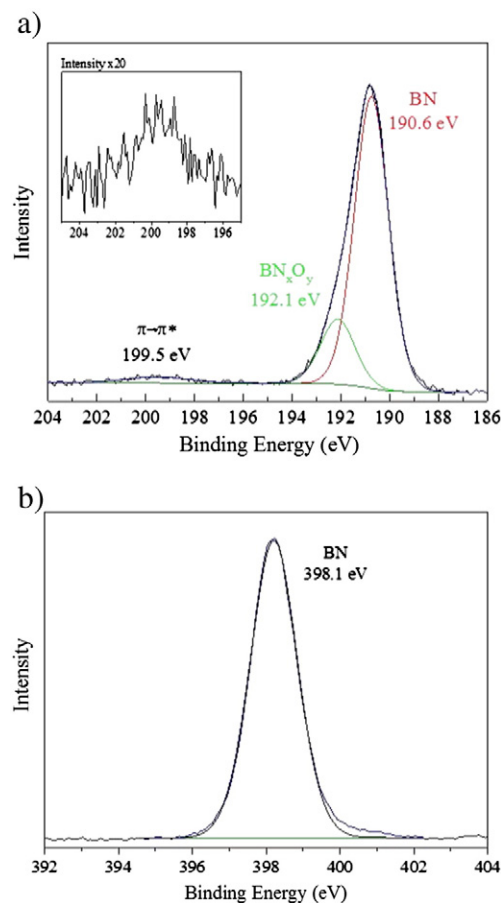

Fig. 2. CCD camera image of plasma emission intensities for 3 cm target-to-substrate working distance at various pressures and time after impact of the laser pulse on the target.

Fig. 3. a) Representative XPS scan of the B 1s peak as well as the $\pi \rightarrow \pi^*$ satellite shifted 9 eV from the B 1s peak, and b) a representative scan of the N 1s peak.
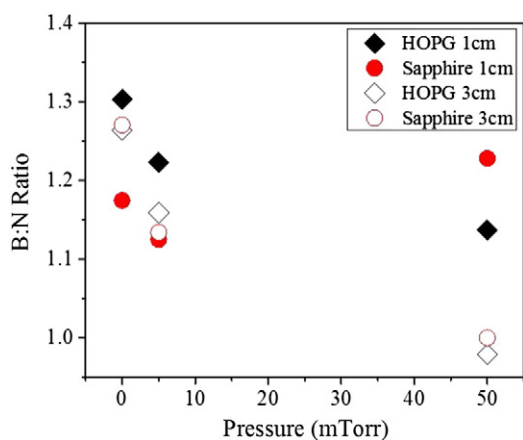
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Fig. 4. Boron to nitrogen ratio as a function of nitrogen background pressure within the deposition chamber.

distance, the increased number of collisions with background gas molecules greatly helped in the formation of stoichiometric BN thin films.

In addition to the lattice parameter difference, a sapphire (0001) surface energy of 1–2 J/m^2 is an order of magnitude larger than that of the HOPG (0001) surface, where 0.1–0.2 J/m^2 values are typical. From this observation, the HOPG surface with a low surface energy will allow for a longer dwelling of mobile species deposited on the surface from the ablated plasma plumes and a better opportunity for crystalline h-BN formation. The E$_{2g}$ shear mode, characteristic of h-BN [17], is visible at 1362 cm^{-1} of samples grown on the HOPG substrates only, as seen in Fig. 5a. Peaks in the Raman spectra of h-BN on HOPG include the highly ordered G, G*, and G′ bands of HOPG at 1581 cm^{-1}, 2440 cm^{-1}, and 2725 cm^{-1}, respectively. The D band of highly ordered graphite (1352 cm^{-1}) is not evident in scans prior to deposition, as the substrates are very highly ordered, and does not show up post-deposition. The latter is an important observation, as one of the concerns for thin film growth with PLD is a potential substrate damage and defect generation due to the energetic particle bombardment. The background gas collisional deceleration of the ablated plasma in this study had helped to reduce the kinetic energy of the arrival species to below 7–8 eV de-cohesion energy for carbon atoms from the HOPG surface [28]. The observed crystalline h-BN Raman signature for the growth on the HOPG substrate further corroborates the XPS π → π* satellite, suggesting epitaxial-like growth on the lattice matched interface, which was not evident on the sapphire. Similar epitaxial-like growth has been exhibited by cubic boron nitride films on the nearly latticed matched diamond (0001) surface [29].

The different working distances appear to influence the Raman response distribution of grain boundaries, as seen in Fig. 5a. The longer working distance results in a smaller FWHM for the E$_{2g}$ Raman peak, indicating a larger average grain size within the polycrystalline material. The extremely high intensity Raman shift of the G peak results in an asymmetric h-BN Raman response, making estimation of the FWHM difficult to determine. To correct for this, a background subtraction of the pristine HOPG wafer from the BN Raman signal was performed. The FWHM for the most crystalline sample at 3 cm WD and 50 mTorr was 58 cm^{-1}, indicating an average in-plane domain size to be 2.9 nm for the most crystalline BN film grown at 700 °C on an HOPG substrate, as compared to other polycrystalline BN films [30].

AFM topographical scans indicated large-area film coverage and do not exhibit formation of micron-sized domains of BN, as is the case in many CVD grown BN films [31,32]. The RMS roughness of the BN films
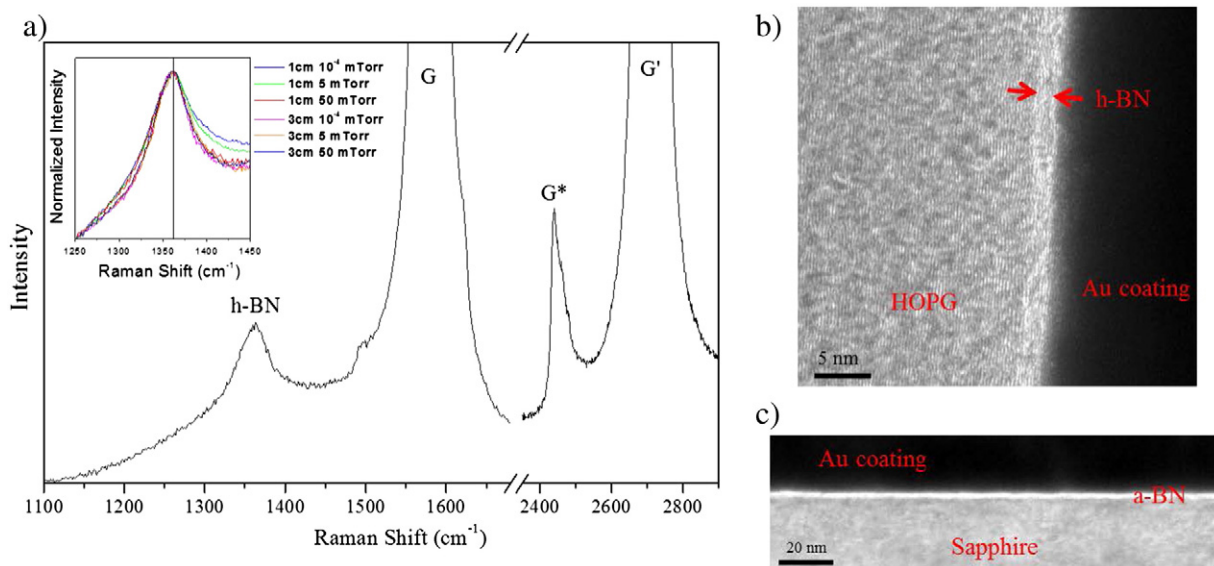
grain edges. The N 1s peak is fit with a single component at 398.1 eV. High resolution spectra of the B 1s region for films grown on HOPG also revealed a broad satellite peak at 9 eV higher binding energy from the main B 1s line [27]. This energy difference is characteristic of the π → π* transition in h-BN and was only observed for the films grown on HOPG. The crystalline formation on only the lattice matched sp^2 bonded carbon phase indicates an epitaxial-like growth phenomena, where the incoming flux of deposited species has sufficient energy and surface diffusion time to restructure and match the structural template of the substrate material at the condensation surface.

Fig. 4 displays the boron-to-nitrogen ratios, calculated from the XPS data, as a function of both working distance and pressure for PLD grown thin films of boron nitride. The B:N ratio decreases with increasing pressure for all deposited films, with the exception of those prepared on sapphire at 1 cm working distance. The decrease in the ratio indicates a more stoichiometric construction of the films as the number of collisions between the plasma and the background gas increases. Independent of the substrate material, a 1:1 B:N stoichiometry is observed in films grown at greater working distance and at 50 mTorr background pressure. The interaction with the background gas at this pressure appears to optimize generation of BN at the interface between the plasma and substrate. In addition to the proper target-to-substrate working

Fig. 5. a) Raman spectra from polycrystalline h-BN on HOPG, and the inset shows the normalized intensity of the E$_{2g}$ shear mode as a function of nitrogen background pressure; b) cross-sectional TEM image of approximately 2 nm, polycrystalline h-BN on HOPG; and c) ultra-smooth amorphous boron nitride on crystalline sapphire (0001).

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was independent of deposition pressure conditions, and yielded an average of 0.493 nm on HOPG and 0.133 nm on sapphire for a given 4 μm^2 area.

To confirm the film thickness and crystallinity, the samples were cross sectioned and studied with transmission electron microscopy (TEM). Determination of thickness of the crystalline BN films on HOPG via TEM proved difficult due to similar e beam absorption coefficients and very close inter plane lattice spacing between of these materials. Nevertheless, the TEM image in Fig. 5b clearly indicates a surface layer, where due to the atomic mass contrast an ordered surface layer was determined as that of h BN, and the thickness was estimated to be 2 nm, or about 6 atomic layers. Similarly to XPS and Raman spectros copy results, TEM studies also confirmed that amorphous BN films were grown on sapphire. The film thickness was approximately 2 nm when grown at 50 mTorr, with large area coverage and no evidence of pin holes within the amorphous film (Fig. 5c).

Complementary to TEM, h BN thickness estimations were per formed utilizing XPS data based upon the exponential decay of substrate photoelectrons with increasing overlayer thickness due to inelastic scattering effects. Atomic concentration ratios between unique, non interfering photoelectron peaks from the overlayer (B 1s, N 1s) and the substrate (C 1s, Al 2p) were fit to a homogeneous, flat overlayer model incorporating the inelastic mean free paths (IMFPs) of substrate photoelectrons within the substrate, substrate photoelectrons within the overlayer, and overlayer photoelectrons within the overlayer in order to determine an effective overlayer thickness. This method has been detailed elsewhere [33,34]. The data confirmed film thicknesses of 1.6 nm on HOPG and 2 nm on sapphire and show that PLD offers good control over film thickness for macroscopic length scales, as the XPS analysis spot size was at 800 μm in diameter. TEM and XPS thick ness measurements were repeated in multiple locations over the 5 mm × 5 mm sample area, yielding the same results at each spot. It is known from PLD literature that the process allows for good film unifor mity, and with the addition of beam rastering and sample motion, larger area samples can potentially be accommodated with similar large area uniformity as those seen in this study [35].

Fig. 6 shows eight C AFM scans on the PLD grown h BN films per formed over the 5 mm × 5 mm sample that indicate large area coverage free of pin holes and good electrical performance uniformity. Assuming a 1.8 nm BN film, the average low biased tunneling resistance (R_{LB}) for the polycrystalline h BN film is 1.811 Ω/m, calculated by the slope of the low bias regime, as seen in the inset of Fig. 6. The polycrystalline film will most likely exhibit a different electrical response from a pris tine flake due to inherent grain boundaries within the film, resulting in slightly differing low bias I V characteristics. Pristine h BN flakes have shown to have a high dependence of low biased tunneling

resistance on thickness, in the range of 0.5 Ω/m for 1 nm thick flakes to 100 Ω/m for 2 nm thick flakes [36].

4. Conclusions

PLD has been investigated as a new approach for the synthesis of ultra thin boron nitride films in contrast to currently used CVD process es. This technique has been shown to produce stoichiometric, polycrys talline four to six layer BN films within 5 s of deposition on 25 mm^2 areas at 700 °C temperatures. This was achieved by in situ recording and adjusting pulsed plasma plume evolutions to optimize growth con ditions at the condensation surfaces with the presence of reactive, ther mally excited, high mobility, and long diffusion time species on the condensation surface. Growth of crystalline h BN on both lattice matched substrates (e.g., HOPG) as well as amorphous, smooth a BN films on crystalline substrates (e.g., sapphire) was demonstrated with complete coverage of the large area without pinholes, or any other cross thickness defects as confirmed with a number of techniques. When compared to traditional CVD methods, the technique opens up the possibility of preparing high quality BN films on a wide range of substrates previously incompatible with traditional BN growth methods, as well as the potential to scale the film production to large areas, with the high throughput required for commercialization.

Acknowledgments

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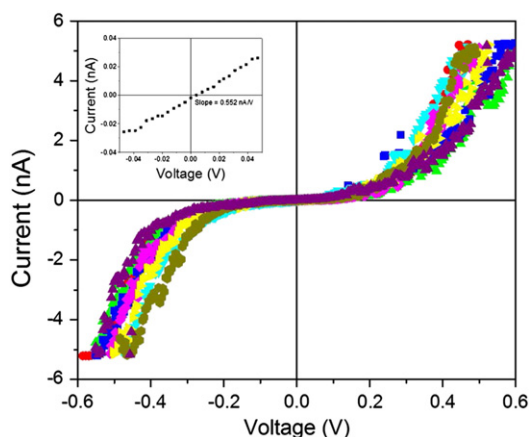
Fig. 6. Conducting AFM I–V curves of eight spots on a 5 mm × 5 mm BN-coated HOPG sam ple, and the inset shows the average value of the low-biased tunneling curve.

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